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(54) LIVING ANIONIC POLYMERS GRAFTED TO COPOLYMERS OF LOWER OLEFINS AND ACRYLATE ESTERS

(71) We, GULF OIL CORPORATION, a Corporation organized under the laws of the State of Pennsylvania, United States of America, of Gulf Building, 7th Avenue and Grant Street, Pittsburgh, Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to graft polymers.

The invention also relates to a method of preparing a graft polymer.

The term "living" polymerization is a term of art which describes the phenomenon whereby under certain conditions certain monomers are capable of forming polymer chains of theoretically infinite length, i.e., they do not terminate spontaneously by monomer termination but will continue to grow as long as there is any monomer present in the polymerization mixture to form a polymer chain. This polymer chain is essentially stable even though it contains an active site at the growing end, but, if more monomer is added, will resume its growth until the newly added monomer is consumed.

According to the present invention there is provided a graft polymer of a living anionic polymer grafted onto a backbone of a copolymer of an olefin or diolefin having from 2 to 6 carbon atoms and an ester of an α/β -unsaturated carboxylic acid.

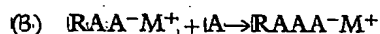
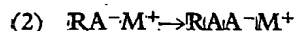
Preferably the living anionic polymer is polystyryl or polybutadienyl.

The living polymerization is initiated by contacting the monomer, suitably in a liquid medium, with an anionic polymerization initiator, preferably in an amount of from 0.0001 to 1.0 moles per mole of monomer, such as a metatorganic compound, which yields a carbanion, viz.,



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and chain-growth occurs by the mechanism 45



until the supply of monomer is exhausted. In the above equations A represents the monomer, R and M respectively represent the organic and metal moieties of the polymerization initiator, R⁻ being the carbanion and M⁺ being the counterion. It will be noticed that as the chain grows the active anionic site is continually transferred to the end of the chain so that the living polymer itself becomes the carbanion which initiates further chain growth.

The particular anionic polymerization initiator which is employed will depend to some extent upon the particular "A" monomer being polymerized, but will generally correspond to those catalysts which are art-recognised as capable of initiating the living polymerization of the monomer. As specific examples of common anionic polymerization initiators which can be successfully employed in the practice of this invention may be mentioned alkali metals and compounds of alkali metals, aluminium and zinc. Examples of these initiators are lower alkyl lithiums such as butyl lithium, 9-fluorenyl lithium, amyl sodium, potassium naphthalenide, sodium metal, phenyl lithium, alkali metal hydrides, e.g., sodium hydride, aluminum alkyls and zinc alkyls, e.g., aluminum triethyl, aluminum triisopropyl, zinc dimethyl, zinc diethyl and zinc dibutyl. By the term "lower alkyl", as used herein and in the claims, is meant an alkyl group of not more than 6 carbon atoms.

In general any of the reactive ethylenically unsaturated polymerizable monomers which can be polymerized by the use of an anionic initiator to form a stable carbanionic polymer without a chain termination step can be employed to form the "A" polymer in the practice of this invention. For example, such diverse monomers of this type as styrene, butadiene,

alpha-methyl styrene, methyl methacrylate, n-butyl methacrylate, isoprene, acrylonitrile, methacrylonitrile and N,N-di-n-butylacrylamide can be used.

5 The carbanionic "A" polymers are prepared in the practice of this invention by the methods generally known and employed in the art with the further qualification that the polymeriza-
10 tion of the "A" monomer should be conducted under conditions which minimize chain transfer and chain termination so as to produce the largest number of living polymer chains. Preferably the polymerization is carried out
15 in a liquid medium, which medium is capable of dissolving both the monomer and the polymer under very mild conditions of temperature, e.g., -70°C . to $+110^{\circ}\text{C}$., and at atmospheric pressure. Extreme care should be
20 exercised to maintain the polymerization system essentially free of impurities which would cause chain transfer or chain termination. To this end it is desirable to employ high purity monomers, reaction medium liquids, catalysts, etc. Water, oxygen and commonly employed
25 inhibitors are especially troublesome impurities which should preferably be carefully excluded. In general any active hydrogen compounds should be excluded.

30 Examples of the copolymer used are ethylene-methyl acrylate, ethylene-methyl methacrylate, butadiene-methyl acrylate, butadiene-methyl methacrylate, isoprene-methyl methacrylate and isoprene-methyl
35 acrylate. The olefins used are the C_2 to C_6 olefins or diolefins, and preferably C_2 to C_4 olefins. The esters of α - β unsaturated carboxylic acids which may be used are preferably the acrylates and methacrylates, but the fumarates, itaconates and maleates may also
40 be used.

45 It is known in the prior art to graft the living polystyryl anion to the rigid copolymer of styrene and methyl methacrylate. Other graft copolymers have been studied for a number of years and some of the products are of commercial importance. Perhaps one of the most noteworthy of these is the ABS family
50 of resins which are complex products containing graft polymers of acrylonitrile, butadiene and styrene. The usual method of preparing graft polymers involves polymerization of a monomer in the presence of a preformed
55 (backbone) polymer using a free radical initiator. This method invariably leads to a mixture of graft copolymer and homopolymer since a complex series of reactions is occurring simultaneously.

60 Considerable time and effort have been spent in the past to obtain a high-impact strength plastic by grafting styrene onto ethylene-acrylic copolymers using the free radical initiators. These efforts met with little success since the efficiency of grafting was extremely low. In
65 fact, grafting efficiencies greater than 20 per cent were seldom achieved. The prior art

faced a problem of preparing a graft polymer, with high grafting efficiency, of a rigid, brittle, hard, high tensile strength, low elongation polymer, such as polystyrene or styrene copolymers, and a flexible, non-brittle, low tensile strength, high elongation polymer such as polyolefins or olefin copolymers. Such a product would be competitive with the ABS resins as a molding resin or high-impact strength plastic. Such a product could also
70 be made at a lower cost than the ABS-type resins.

The graft polymer may be prepared by simply mixing the living anionic polymer with the copolymer in a solvent under extremely
80 clean conditions. The impurities discussed above for the preparation of the living anionic polymer cannot be present when the graft polymer is prepared. The solvents which can be used are any solvents which will dissolve
85 both reactants, such as the higher aliphatics, and the aromatics, preferably the aromatics, such as toluene and xylene. Chlorinated solvents are not operable, since they react with dissolved reactants. As pressure is not critical, the reaction is usually run at atmospheric pressure, but will also take place at higher pressures or under vacuum. The graft polymer
90 can be prepared in a batch or in a continuous process. The temperature of the grafting reaction is limited only by the solubility of the reactants and the boiling point of the solvent. The reaction will occur at any temperature
95 above the temperature at which one of the reactants precipitates out of solution, up to the temperature at which the solvent boils. The preferred temperature range is from the temperature just above the temperature at which precipitation of one of the reactants
100 occurs to below 60°C . For example, a 5% solution of ethylene-methyl methacrylate copolymer (24 weight per cent methyl methacrylate) in a solvent mixture of 90% toluene 10% tetrahydrofuran will precipitate copolymer at about -10°C . A 5% solution of ethylene-methyl acrylate copolymer (19 weight per cent methyl acrylate) in a solvent mixture of 90% toluene, 10% tetrahydrofuran will precipitate
105 copolymer at about 12°C .

A method has now been found to prepare a graft polymer compound from a rigid, brittle, hard, high tensile strength, low elongation polymer and a flexible, non-brittle, low tensile strength, high elongation polymer with nearly
110 100 per cent grafting efficiency. The method comprises mixing living polymer anions prepared by the well-known methods with an olefin-acrylate copolymer under anhydrous and oxygen-free conditions. This method can also be used to produce graft polymers of two
115 120 flexible materials. The living polymer anion reacts quantitatively with the ester groups on the copolymer. One advantage of this invention is that it is specific and quantitative. Another advantage is that the length and number
125 130

of living polymer anion chains grafted to the copolymer backbone can be rigorously controlled. Thus, a wide variety of graft copolymers can be prepared, while maintaining complete control of the composition on a molecular scale.

These graft polymers of a flexible polymer and a rigid polymer have improved abrasion resistance, elongation, flexibility and impact resistance when compared to the rigid, brittle, hard, high tensile strength, low elongation polymers, and have improved stiffness, hardness, tensile strength, bulk properties, and heat distortion properties when compared to the flexible, non-brittle, low tensile strength, high elongation polymers.

The graft polymers of a flexible polymer and a rigid polymer of this invention are thermoplastic and useful as molding resins and high-impact strength plastics. Their uses are similar to the commonly known ABS resins.

The graft polymers of two flexible materials can be used to prepare polymeric foams unknown in the prior art. The foams produced are useful anywhere padding or insulation is needed.

The reactants and products from the experiments involving the grafting of living polystyryl anion to ethylene-methyl methacrylate copolymers are shown in Table I.

Toluene and tetrahydrofuran were distilled over NaH under argon directly into the polymerization vessel. Styrene monomer was passed through calcined alumina and collected in a vessel under argon. n-Butyl lithium as a 22% solution in hexane (Aldrich Chemicals) and ethylene-methyl methacrylate copolymer, containing 24% methyl methacrylate were used as supplied.

The polymerization vessel, a 2-litre, 4-neck flask, was dried, then flamed under argon to remove occluded oxygen. Both toluene and tetrahydrofuran were distilled into the vessel followed by the styrene monomer, added via syringe. The vessel was cooled to -40°C . and n-butyl lithium was added dropwise to kill initial impurities (0.75 mm and 0.45 mm required for Example 1 and Example 2, respectively) until a characteristic yellow color remained at which time the mole per cent as shown in Table I required to give a molecular weight of 10,400 (DP of 100) was added all at once, giving the characteristic dark orange color of the polystyryl anion. The polymerization was allowed to proceed for 3 to 4 hours.

In Example 1 the actual graft was carried out by the addition of the ethylene-methyl methacrylate copolymer solution (5% in toluene) via addition funnel to the polystyryl lithium in toluene/tetrahydrofuran, whereas in Example 2 the grafting operation was carried out by transferring the living polystyrene by

argon pressure through a dip tube to another flask containing the ethylene-methyl methacrylate copolymer solution in the same closed system. In both experiments, butyl lithium was added to the ethylene-methyl methacrylate copolymer solution, 2.0cc/12g. (Example 1) and 1.0cc/25g. (Example 2), prior to the actual grafting operation in order to remove any reactive impurities present. In Example 1 this resulted in the precipitation of about 5.2 g. of ethylene-methyl methacrylate copolymer and as a result only 150 ml of the solution containing about 4.1 g. of ethylene-methyl methacrylate copolymer were added. Upon addition of the n-butyl lithium to both solutions a slight increase in viscosity coupled with a slight temperature increase from 24°C . to 30°C . was noted.

In Example 1 the ethylene-methyl methacrylate copolymer solution was added to the living polystyrene solution at -5°C . and was allowed to warm to room temperature. At the end of one hour the characteristic color of the polystyryl anion had vanished indicating complete reaction. In Example 2 the grafting was performed at room temperature with the characteristic orange color lost as soon as the living polystyrene was added to the ethylene-methyl methacrylate copolymer solution.

Both reactions were quenched and their products isolated in methanol and dried in vacuo at 55°C . for 24 hours.

The products from Examples 1 and 2 were extracted with acetone (a solvent for polystyrene) and the insolubles were dissolved in dioxane at 80°C . It had been previously established that ethylene-methyl methacrylate copolymer is insoluble in dioxane under these conditions. The results are shown in Table II. These data indicate that styrene grafting efficiency was very high and that no ungrafted ethylene-methyl methacrylate copolymer remained. Molecular weight measurements on the styrene homopolymers extracted indicate that these chains were terminated during the transfer step by acidic impurities remaining in the ethylene-methyl methacrylate copolymer solution.

The intrinsic viscosity of the graft polymer from Example 2 is shown in Table III, along with the values for the polystyrene homopolymer (methanol terminated), ethylene-methyl methacrylate copolymer and a physical blend of ethylene-methyl methacrylate copolymer and homopolymer.

Examples 3 and 4 were carried out exactly as Example 2. For Example 3, the backbone polymer was a low molecular weight ethylene-methyl methacrylate copolymer containing 40% methyl methacrylate. The graft polymer from Example 4 contained only 32% styrene and was flexible and tough.

TABLE I

Preparation of Styrene/Ethylene-
Methyl Methacrylate Copolymer Graft Copolymers

Polymerization Conditions	Example 1	Example 2	Example 3	Example 4
Monomer	Styrene	Styrene	Styrene	Styrene
Amount (g.)	81.0	80.0	73.5	40.0
Amount (moles)	0.78	0.77	0.71	0.385
Catalyst	BuLi ^(a)	BuLi	BuLi	BuLi
Amount (ml)	3.29	3.13	2.9	1.6
Amount (moles)	0.0078	0.0077	0.0071	0.00385
Solvent	Toluene/THF	Toluene/THF	Toluene/THF	Toluene/THF
Amount (ml)	950/50	760/40	700/30	400/20
Temperature (°C)	-40 to 0	-40 to 0	-40 to 0	-40 to 0
Time (hrs.)	3	4	2	2.25
Grafting Conditions				
Copolymer (E/MMA, wt %)	76/24	76/24	60/40	76/24
Amount (g.)	12.0 ^(b)	25.0	30.0	60.0
Solvent	Toluene	Toluene	Toluene	Toluene
Amount (ml.)	250	500	600	1200
Temperature (°C.)	-5 to 24	24	15-24	20-24
Time (hrs) ^(d)	1.0	Immediate	Immediate	Immediate

TABLE I (Continued)

Preparation of Styrene/Ethylene-
Methyl Methacrylate Copolymer Graft Polymers

Product	Example 1	Example 2	Example 3	Example 4
Yield (g.)	84.8	103 ^(c)	85.65 ^(e)	97.2
Graft Copolymer (After Extraction)				
Yield	94.7	89.8	—	84.3
PS/Copolymer (wt %)	95/5	73.5/26.5	—	32/68
Softening Point (°C.) (Fisher-Johns)	94	98	105	144

(a) Supplied as a 22% solution in hexane (Aldrich Chemicals).

(b) 4.1 g. in 150 ml were added.

(c) 2.2 g. of polystyryl lithium left in reactor quenched in methanol for molecular weight determination.

(d) Time to loss of orange color.

(e) 2.79 g. of polystyryl lithium left in the reactor quenched in methanol for molecular weight determination.

TABLE II
Resolution of Products into
Homopolymers and Graft Copolymer

Extraction ^(a)	Extraction Conditions(b)	Example 1 Wt. %	Example 2 Wt. %
Original Sample	—	100	100
Styrene Homopolymer	Acetone sol., 40°C.	6.3	10.2
Ethylene-Methyl Methacrylate Copolymer	Dioxane insol., 80°C.	0	0
Residue (Graft Copolymer)	—	94.7	89.8

(a) Extraction products characterized by infrared analysis.

(b) The products were run in each solvent until the subsequent extraction revealed no further polymer.

TABLE III
Solution Properties of Styrene Graft
Polymer from Example 2 in Benzene,^(a) 30°C.

Sample	$[\eta]$	$\bar{M}_n^{(b)}$
Polystyrene ^(c)	0.11	12,040 ^(e)
PS/Ethylene-Methyl Methacrylate, Copolymer, 72/28, Physical-Mixture ^(d)	0.33	—
Product (before extraction)	0.60	—
Graft Polymer	0.64	—
Ethylene-Methyl Methacrylate Copolymer	0.85	—

(^a) Sample concentrations at 0.25 g/dl., 0.5 g/dl. and 1.0 g/dl.

(^b) The equation $[\eta] = 9.7 \times 10^{-5} M^{0.74}$ was used.

(^c) 2.2 g. polystyrene removed from reactor prior to grafting.

(^d) Polystyrene from reactor used in mix.

(^e) The calculated value is 10,400.

EXAMPLE 5.

The experiment involving grafting of living polystyryl anion to butadiene-methyl methacrylate copolymers is described as follows:

5 The reactions were carried out in two 3-neck flasks joined together with ground joints in such a way that the contents of one could be transferred to the other one by rotation of the joints. The flasks were fitted with other
10 accessories to permit the inflow and outflow of an inert gas to allow the addition and removal of materials from the flasks without exposure to the atmosphere.

All of the reaction apparatus was first
15 treated to remove materials capable of reacting with styryl lithium. It was washed thoroughly with water, washed with acetone and dried overnight in an oven at 150° C. The apparatus was assembled while warm,
20 and further heated with hot air from a "heat gun" while inert gas, argon, was flowing through it.

Into one flask was put 2.8 grams (0.00524
25 mols of ester groups), butadiene-methyl methacrylate copolymer, containing 18.7 weight per cent of methyl methacrylate, 28 ml of specially purified toluene, and 0.3 grams of a sodium dispersion in petrolatum. This mixture was stirred magnetically until the copolymer
30 dissolved. In the other flask was put 200 grams of toluene and 50 grams of styrene (0.480 mol). The toluene was freshly distilled from sodium hydride under an inert gas. The styrene was purified by passing it through a
35 column of absorptive alumina.

To remove residual impurities *n*-butyl lithium solution was titrated into the styrene-toluene solution until the yellow-orange color of the styryl anion persisted. Following this,
40 1 ml. of *n*-butyl lithium solution (0.00242 mole) was added. This solution was stirred for 2.5 hours at 30° C., during which time the viscosity increased considerably. A portion of this solution, 34.8%, was removed and injected into methanol to precipitate the polystyrene produced. This sample was taken to
45 determine the kind and amount of polystyrene added to the copolymer.

The remaining polystyryl lithium solution
50 was mixed with copolymer solution at 30° C. Almost immediately on mixing the orange color disappeared and a large increase in viscosity was produced. After mixing overnight at room temperature, the solution was
55 stirred into several volumes of methanol to precipitate the graft polymer. The precipitate was rigorously washed several times in methanol and finally dried in a vacuum oven. The amount of dry polymer recovered was
60 33.0 grams, or 93.3 per cent of that theoretically possible.

Intrinsic viscosity measurements on the graft polymer gave a value of 0.428, and on the polystyrene portion a value of 0.178. This

gives a molecular weight for the polystyrene block of 16,800 grams/mol. 65

To show that the polystyryl anions had grafted on to the copolymer chains rather than forming polystyrene homopolymers the graft product was carefully extracted with
70 boiling acetone. Infrared analysis of the dried extract and the graft polymer showed that between 0% and 3% of the polystyrene was homopolymer. The analysis showed that
75 40.5% of the ester groups in the copolymer had reacted.

The sodium dispersion was added to the copolymer solution to react with residual impurities that might destroy the styryl anions, while leaving the ester groups free to react
80 with the polystyryl anions. The analytical data indicate that the desired results were effectively achieved.

EXAMPLE 6.

The experiment involving grafting of living polystyryl anion to ethylene-methyl acrylate
85 copolymers is described as follows:

Styrene monomer (60.0 g., 0.577 mol) was dissolved in a mixture of 480 ml of toluene and 60 ml of tetrahydrofuran. The solution
90 was cooled to 5° C. and polymerization was initiated by addition of 0.00635 mol of *n*-butyl lithium. After 1.5 hr. the temperature was 32° C. A portion of the polystyryl lithium solution (150 ml) was then added under an
95 inert atmosphere to a stirred solution of 10 g. of ethylene-methyl acrylate copolymer (20% by weight methyl acrylate/80% ethylene by weight, 2 melt index) dissolved in 250 ml of
100 toluene. The orange color of the polystyryl lithium faded immediately. After pouring the polymer solution into methanol, the solid product was isolated by filtration and washed several times with fresh methanol. The yield
105 was quantitative. Compression moldings were flexible and opaque.

EXAMPLE 7.

The experiment involving grafting of living polybutadienyl anion onto ethylene-methyl
110 acrylate (20% by weight methyl acrylate/80% by weight ethylene, 2000 melt index) is described as follows:

Butadiene (118.6 g. of Phillips Petroleum Research Grade, purity, 99.88 mole percent)
115 was purified by passing the gas through 4A molecular sieves and charged to a pressure bottle containing 300 ml. of toluene. After purging with argon, *ni*-butyllithium (0.7 ml. of 22% in hexane) was added and the reaction mixture heated with stirring to 50° C.
120 The top was removed in the inert atmosphere and 150 ml. of the "living" polymer solution was poured into a dry, oxygen free solution of 22.5 g. of ethylene-methyl acrylate copolymer in 335 ml. of toluene containing 10%
125 tetrahydrofuran. The reaction mixture was

stirred for 30 min. before it was removed from the dry box. The product was precipitated by pouring into methanol and isolated by filtration. Antioxidant was added and the product was dried in a vacuum oven at 30° C. The yield was 30.1 g.

WHAT WE CLAIM IS:—

1. A graft polymer of a living anionic polymer grafted onto a backbone of a copolymer of an olefin or diolefin having from 2 to 6 carbon atoms and an ester of an α - β unsaturated carboxylic acid.

2. A graft polymer according to claim 1 wherein the living anionic polymer is polystyryl.

3. A graft polymer according to claim 1 wherein the living anionic polymer is polybutadienyl.

4. A graft polymer according to any one of claims 1 to 3 wherein the said copolymer is an ethylene-methyl acrylate copolymer.

5. A graft polymer according to any one of claims 1 to 3 wherein the said copolymer is an ethylene-methyl methacrylate copolymer.

6. A graft polymer according to any one of claims 1 to 3 wherein the said copolymer is a butadiene-methyl methacrylate copolymer.

7. A process for preparing the graft polymer claimed in any one of claims 1 to 6 comprising mixing a monomer of an anionic living polymer with a living anionic polymerization initiator to form a living anionic polymer and reacting said polymer with a copolymer of an olefin or diolefin having from two to six carbon atoms and an ester of an α , β -unsaturated carboxylic acid.

8. A process according to claim 7 wherein said mixing takes place in an anhydrous solvent under an inert gas and under clean conditions.

9. A process according to claim 7 or 8 wherein the initiator is used in an amount of from 0.0001 to 1.0 moles per mole of said monomer.

10. A process according to claim 7, 8 or 9 wherein said reacting takes place at a temperature above the temperature at which said copolymer or said living anionic polymer precipitates from the said solvent and below 60° C.

11. A process according to any one of claims 7 to 10 wherein said initiator is a lower alkyl lithium.

12. A process according to any one of claims 7 to 11 wherein said initiator is normal butyl lithium.

13. The process of grafting a living anionic polymer onto a backbone of a copolymer of an olefin or diolefin having from two to six carbon atoms and an ester of an α , β -unsaturated carboxylic acid according to any one of the Examples.

14. A graft polymer whenever prepared by the process claimed in any one of claims 7 to 13 as herein described.

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